

1601818

(21) Application No. 26810/77 (22) Filed 27 June 1977 (19)

(23) Complete Specification filed 30 May 1978

(44) Complete Specification published 4 Nov. 1981

(51) INT. CL.³ C07C 31/02 29/16

(52) Index at acceptance

C2C 20Y 229 30Y 360 361 36Y 408 413
414 416 507 509 623 66Y FF YK(72) Inventors JOHN ERIC LARSON and
GORDON HOWARD WHITFIELD

(54) PRODUCTION OF ALCOHOLS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

THIS INVENTION relates to the production of alcohols.

According to the invention alcohols suitable for the production of plasticisers for polyvinyl chloride by esterifying them with phthalic acid or anhydride are produced by a process which comprises the steps of,

(a) recovering from a paraffinic residue which is derived from the extraction of aromatic compounds from reformed naphtha by solvent extraction, a mixture of paraffins of which at least 75% and preferably at least 90% by weight have carbon numbers in the range 6—10, (the first mixture),

(b) partially dehydrogenating the said first mixture to produce a second mixture comprising 2.5 to 25% and preferably 10 to 20% by weight of olefins and 60 to 95% by weight of paraffins,

(c) optionally concentrating the olefins of the mixture, preferably by adsorption with a selective adsorbent or by extractive distillation to produce a third mixture comprising 15 to 95% by weight of olefins and 3 and preferably 5 to 85% by weight of paraffins, and, if desired, recycling a paraffinic product reduced in olefinic content to stage (b),

(d) hydroformylating the second and/or third mixture to produce aldehydes and/or alcohols,

(e) hydrogenating the aldehydes of stage (d) if necessary to produce alcohols, and
(f) separating paraffins and optionally aromatic compounds from the aldehydes or alcohols.

The second or third mixtures, if need be, may be partially hydrogenated under condi-

tions such that diolefins if present are preferentially reduced.

If desired the paraffins recovered from the aldehydes or alcohols may be recycled to the dehydrogenation stage.

Narrow cuts of paraffin having predominantly for example 6, 7 and 8 carbon atoms are very suitably used in the process as the corresponding alcohols produced will have a carbon number of about 8; such alcohols are very suitable for the manufacture of their phthalates as plasticisers for polyvinyl chloride.

The first mixture may be partially dehydrogenated by contacting it with catalysts for example comprising platinum on alumina at a temperature in the range 400 to 600°C and a pressure in the range 0.1 to 10 bars in the presence of 1 to 20 moles of hydrogen per mole of hydrocarbon.

The concentration of the olefins from the second mixture may be carried out using a selective adsorbent for example the silver form of a 13X molecular sieve. The mechanical techniques for achieving separations with the aid of selective adsorbents are known and have been employed commercially for example in the recovery of normal paraffins from hydrocarbon mixtures containing them.

If desired the first mixture may be recovered from the paraffinic residue by a process which comprises increasing its proportion of normal paraffins using molecular sieves in known manner as the corresponding normal alcohols confer attractive properties on phthalate esters used for plasticising polyvinylchloride. However, the constitution of such residues normally renders this unnecessary.

The hydroformylation of the second or third mixture may be carried out under similar conditions to those employed using substantially pure olefinic feedstock in hydroformylation processes. The paraffins and any aromatics pass through the process

50

55

60

65

70

75

80

85

90

unconverted and have no appreciable adverse chemical effect. The aldehydes may be reduced to alcohols by hydrogenation in known manner; the presence of the paraffinic 5 and any aromatic material has no appreciable deleterious chemical effect in this step either.

The separation of the paraffins and optionally aromatics from alcohols or aldehydes is more easily carried out by distillation than the separation of the olefins from paraffins and the aromatics. It is thus advantageous not to attempt too complete a concentration of olefinic feed stock in stage (c) 10 and if desired this step may be omitted. It is desirable however not to attempt too complete dehydrogenation of the first mixture in step (b) because of the danger of producing unacceptable amounts of diolefines which 15 may be detrimental in the hydroformulation stage.

The invention will now be described with reference to the drawing which shows a flow sheet of a plant for operating the process.

25 122 moles of a paraffinic residue obtained from an aromatics plant is fed by means of line 1 to still 2 from which a bottoms product is fed via line 3 to still 4 from which 100 moles of a top product having a molar 30 composition C_6 hydrocarbons 33%, C_7 hydrocarbons 42% and C_8 hydrocarbons 24% of which normal paraffins constitute 26 molar percent, isoparaffins 68 molar percent, naphthalenes 5 molar percent, and aromatics 1 molar percent, is recovered. The top product 35 is passed by means of line 5 together with 697 moles of a recycle stream supplied through line 6 to a dehydrogenation stage 7 in which the paraffins and isoparaffins are partially 40 dehydrogenated by passing over a platinum on alumina catalyst in the presence of hydrogen gas at 430°C and at one atmosphere total pressure at a gas hourly space velocity of 1300 hours⁻¹. 11 to 12 Molar 45 percent of the paraffins and isoparaffins is converted and the product from dehydrogenation stage 7 contains 10.7 molar percent of mono-olefines, 1.1 molar percent of diolefines, together with about 1 molar percent 50 of aromatics.

The stream from dehydrogenation stage 7 is fed to selective hydrogenation stage 8 in which it is contacted with a palladium on alumina catalyst in the liquid phase at a 55 temperature of 40 to 60°C and at 10 atmospheres pressure in the presence of hydrogen. In this stage the di-olefines are reduced to a level corresponding to a maleic anhydride value of 2 milligrammes per gramme of 60 mono-olefine. The selectively hydrogenated product is then passed to an olefine concentration stage 9 in which it is concentrated by treatment with a selective molecular sieve. In this stage saturated hydrocarbons are selectively removed producing a stream of 65 697

moles of hydrocarbon which is recycled via line 6 to the dehydrogenation stage 7, leaving 100 moles of olefinic concentrate comprising 89 molar percent of mono-olefines, 5.3 molar percent of residual paraffins and 5.7 molar percent of aromatics. The olefinic concentrate is fed to reactor 10 in which it is hydroformulated at 170°C and 250 atmospheres total pressure with a 1:1 molar mixture of hydrogen and carbon monoxide 70 in the presence of 400 parts per million by weight of cobalt catalyst. 86% of the olefine is converted.

75 After removal of the dissolved gases and catalyst the crude hydroformylation product is passed to a hydrogenation stage 11 in which it is contacted with a supported nickel catalyst in the liquid phase at a temperature of 120 to 135°C under hydrogen gas at a pressure of 50 atmospheres, in which the aldehyde components of the crude hydroformylation product are converted to alcohols.

80 The crude alcohol product from hydrogenation stage 11 is distilled in still 12 from which a bottoms product is recovered and further distilled in still 13. A top product (24 85 moles) consisting of hydrocarbons which may be incorporated into gasoline or treated for the recovery of aromatics is also recovered. 63 moles of $C_7/C_8/C_9$ saturated aliphatic 90 alcohol suitable for esterification to phthalate 95 esters to be used as plasticisers for polyvinyl chloride is recovered as the top product from still 13.

100

WHAT WE CLAIM IS:—

1. A process which comprises producing alcohols suitable for the production of plasticisers for polyvinyl chloride by esterifying them with phthalic acid or anhydride the 105 process comprising the steps of,
 - (a) recovering from a paraffinic residue which is derived from the extraction of aromatic compounds from reformed naphtha by solvent extraction, a mixture of paraffins 110 of which at least 75% by weight have carbon numbers in the range 6—10, (the first mixture).
 - (b) partially dehydrogenating the said first mixture to produce a second mixture comprising 2.5 to 25% by weight of olefins and 60 to 95% by weight of paraffins,
 - (c) optionally concentrating the olefins of the mixture to produce a third mixture comprising 15 to 95% by weight of olefins and 3 to 120 85% by weight of paraffins, and, if desired, recycling a paraffin product reduced in olefinic content to stage (b),
 - (d) hydroformulating the second and/or third mixture to produce aldehydes and/or 125 alcohols,
 - (e) hydrogenating the aldehydes of stage (d) if necessary to produce alcohols, and
 - (f) separating paraffins and optionally aromatic compounds from the aldehydes or 130

alcohols.

2. A process as claimed in claim 1 in which the second or third mixtures are partially hydrogenated under conditions 5 such that di-olefines are preferentially reduced.

3. A process as claimed in claim 1 or 2 in which the mixture of paraffins consist predominantly of paraffins having 6, 7 and 8 10 carbon atoms.

4. A process as claimed in claim 1, 2 or 3 in which the first mixture is partially dehydrogenated by contacting it with a catalyst comprising platinum on alumina at a temperature 15 in the range 400 to 600°C and a pressure in the range 0.1 to 10 bars in the presence of 1 to 20 moles of hydrogen per mole of hydrocarbon.

5. A process of producing an alcohol as 20 claimed in claim 1 substantially as described with reference to the accompanying drawing.

T. J. LOCKE,
Agent for the Applicants.

Printed for Her Majesty's Stationery Office by Burgess & Son
(Abingdon) Ltd.—1981. Published at The Patent Office,
25 Southampton Buildings, London, WC2A 1AY,
from which copies may be obtained.

1601818 COMPLETE SPECIFICATION
1 SHEET This drawing is a reproduction of
the Original on a reduced scale

